Development of Chemical Stimuli-responsive Organogel Using Boronate Ester-substituted Cyclotricatechylene

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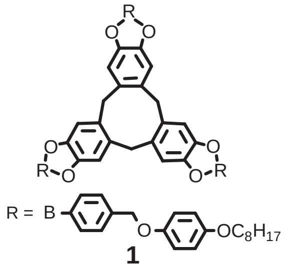
This study describes the synthesis of a new compound: boronate ester-substituted cyclotricatechylene **1**. The structure-directing property of the boronic acid–diol interactions is responsible for the shuttlecock-shaped structure of **1**, which led to the gelation of several solvents. The distribution control of trigonal and tetrahedral boronate esters allows phase transition via chemical stimulus.

Dynamic covalent functionality has been recognized as a powerful mechanism for the construction of organized architectures in supramolecular chemistry.[1] Reversible bond formation enables the thermodynamic control of the reaction under equilibrium so that only the thermodynamically favored entity is formed as the major product. It is also interesting to note that an external chemical stimulus could have a significant effect on the equilibrium of the reaction, which could induce a change in the product distribution; this has motivated researchers to design soft materials. Boronic acids exhibit dynamic covalent functionality, which enables them to rapidly and reversibly form cyclic boronate esters with diols.[2] The formation of these esters has been advantageous in not only the binding of saccharides[3] and polyphenols[4] but also the development of unique architectures such as macrocycles,[5] porous covalent organic frameworks,[6] and polymers.[7] On combining the properties of boronic acids and Lewis acidic boron,[8] self-organized anion chemosensor systems containing diol dye[9] and a dynamic molecular capsule are formed.[10] The latter can be controlled by a pH switch. Although much attention has been currently focused on the preparation of boron-based self-assembly, organogels formed from boronate ester[2] remain to be explored from the standpoint of developing chemical stimuli-responsive smart gels.[11] Here we report the synthesis of a new compound: boronate ester-substituted cyclotricatechylene **1**; it is composed of cyclotricatechylene and 4-(4-octyloxybenzeneoxymethyl)phenylborane. We chose cyclotricatechylene as one of the components of the newly developed compound because it has a rigid and cone-shaped molecular structure that is capable of serving not only as a receptor[12] but also as a skeleton of liquid crystals[13] and organogelators.[14] We reasoned that the C_3-symmetrical catechol segments of cyclotricatechylene could easily participate in boronate esterification to produce our desired system.

The synthesis of **1** was straightforward (Scheme S1[15]) and was observed by NMR and MALDI-TOFMS; $m/z = 1349.632$ $[\mathbf{1} + \mathrm{Na}]^+$, Calcd. for $C_{84}H_{93}B_3O_{12}Na$: 1349.687. Compound **2** was also synthesized as a control.[15] Gelation tests[16] were carried out using conventional solvents (Table S1[15]). It was observed that **1** was insoluble in nonpolar and protic solvents, while it was soluble in several less polar solvents such as toluene, THF, $CHCl_3$, and CH_2Cl_2. Next, it was found that **1** was responsible for the gelation of the solvents. On estimating the critical gelation concentration (CGC) of the solvents, the lowest CGC value was obtained: 0.46 wt % when toluene was used.[17] The morphological analysis of toluene xerogel was performed by field-emission scanning electron microscopy (FE-SEM); a ribbon-phase with a ca. 330 nm width was obtained (Figure 1a). Further, fine striations of 10–20 nm width were clearly observed on the ribbons; this is attributable to the molecular packing of toluene xerogel. The self-assembly of toluene xerogel was analyzed using X-ray diffraction (XRD) (Figure 1b). A sharp d_{10} peak and low-intensity d_{11}, d_{20}, and d_{21} peaks were observed in the XRD spectra. These peaks could be assigned on the basis of a hexagonal columnar aggregate.[18] The diameter a $(=2 \times d_{10}/\sqrt{3})$ of the gel estimated to be 28.5 Å is smaller than the lateral dimension of the shuttlecock-shaped structure of **1**. This difference in size can be explained by intercolumnar interdigita-



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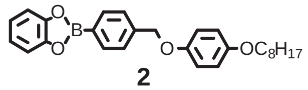

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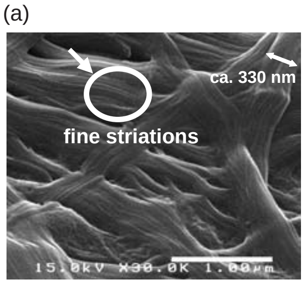

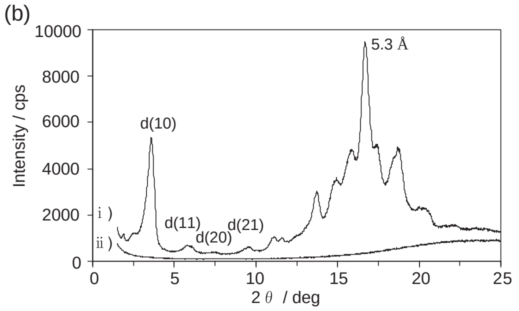

Figure 1. (a) FE-SEM image of xerogel of **1**. The scale bar corresponds to 1.0 μm. (b) XRD pattern of i) xerogel of **1** and ii) blank at room temperature. The xerogels were prepared from toluene (2.5 wt %).

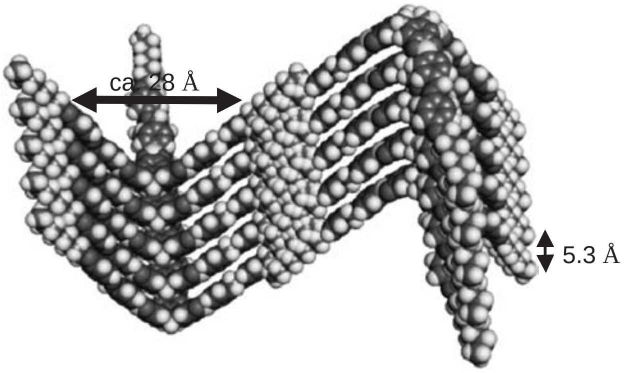

Figure 2. Possible molecular packing structure of toluene gel.

tion of the alkyl chains through van der Waals interactions. A broad peak around 5.3 Å in the wide-angle region of the XRD pattern can be assigned to molecular stacking within the columns. Figure 2 shows a possible molecular packing structure of toluene gel.

As the next stage, we were interested in investigating whether the obtained gel would exhibit a phase transition in response to chemical stimulus such as anions. We reasoned that the chemical stimulus capable of binding trigonal boronate ester in the system would induce a change in its coordination mode, thereby bringing about a change in the morphology of the gel. As a standard examination method, $CHCl_3$ solution (7.5 µL) containing AcO^- (4.5×10^{-3} mmol; 3 equiv for **1**) as tetrabutylammonium salt as putative anions[9a] was added to the toluene gel of **1** (10 mM, 1.5 wt %); the resulting mixture was sonicated for 3 min. Subsequently, the use of AcO^- resulted in a gel-to-sol transition at room temperature (Figure S1[15]), which can be explained on the basis of an anion-triggered $sp^2 \rightarrow sp^3$ conversion of the boron element in **1**. The reaction was also confirmed by the ^1H NMR spectrum of the sol phase. Because of the presence of AcO^-, proton resonances arising from phenyl boronate in **1** were clearly distinguishable signals; one set of the signals is observed at 7.88 (d, $J = 7.5$ Hz) and 7.36 (d, $J = 7.3$ Hz), while a set of broad signals is observed between 7.67–7.46 and 7.23–7.04 ppm (Figure S1[15]). The sol phase may contain disintegrated **1** and acetate-triggered sp^3-boronate derivatives, indicating that the boronate ester segments play a significant role in the gel-to-sol transition. Further, the chemical stimulus-responsive transition is not limited by the addition of anions; when Et_2NH (3 equiv) was used as chemical stimuli under similar conditions, gel-to-sol transition occurred. It is noteworthy that regelation occurred owing to a treatment involving heat under reduced pressure (Figure 3). The removal of Et_2NH enables the reaction equilibrium to shift toward the formation of trigonal boronate ester **1**. Thus, reversible sol–gel transition in the system was achieved.

In conclusion, we present for the first time a boronate-ester-type organogelator which shows a phase transition in response to a chemical-stimulus such as anion and amine. The phase transition is due to a change in the coordination mode of boron in **1**. The results obtained in this study could provide significant information on how boron-based dynamic covalent functionality can be employed to prepare smart gels. The development of an enhanced system having optical functions is in progress according to this strategy.

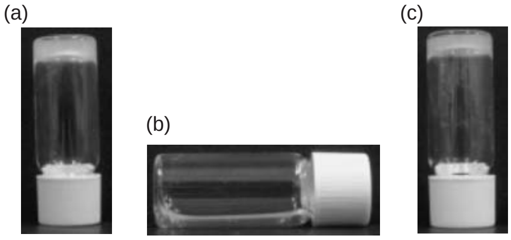

Figure 3. Images of the toluene gel of **1**, which responded to Et_2NH. (a) Toluene gel of **1** (1.5 wt %). (b) Toluene gel of **1** containing Et_2NH (3 equiv for **1**); the gel was then sonicated for 3 min. (c) Solution (b) was evaporated, and its residue was dried at 90 °C in vacuo, cooled, and dissolved in toluene.

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